

**PRODUCTION OF ACRYLAMIDE POLYMER**

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**Abstract**

**PURPOSE:** To obtain the titled polymer useful as a flocculating agent, thickening agent, etc., having improved flocculating performances, solubility, etc., by hydrating acrylonitrile by the action of a bacterium capable of hydrating nitrile to give acrylamide, treating it with active carbon, and polymerizing it.

**CONSTITUTION:** (A) A bacterium such as strain N-771 (FERM P-4445), etc. belonging to the genus *Corynebacterium* is cultivated, and incorporated with sodium chloride injection to give suspension having 0.5-10wt% mold concentration. (B) 0.5-10wt% acrylonitrile is reacted with the suspension at 7-9pH at ice point -15 deg.C for 0.5-10hrs, then, the active carbon is suspended in the aqueous reaction solution and stirred, or the aqueous reaction solution is fed to the active carbon layer, made to flow out, so that it is treated with the active carbon. It is directly used or after it is adjusted to preferably 5-40wt% acrylamide concentration, and it is polymerized at 0-100 deg.C by the use of a radical initiator (e.g., hydrogen peroxide, etc.), to give the aimed polymer.

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⑩ 発明の名称 アクリルアミド系重合体の製造方法

⑪ 特 願 昭59-235106

⑫ 出 願 昭59(1984)11月9日

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明 細 書

1. 発明の名称

アクリルアミド系重合体の製造方法

2. 特許請求の範囲

ニトリル水和能を有する微生物の作用により水性媒体中でアクリロニトリルを水和して得られるアクリルアミド水溶液を活性炭で処理し、このアクリルアミド単量体またはこれを主体とする単量体混合物を重合することを特徴とするアクリルアミド系重合体の製造方法。

3. 発明の詳細な説明

産業上の利用分野

本発明は、アクリルアミド重合体の製造方法に関するものである。さらに詳しくは、ニトリル水和能を有する微生物の作用によりアクリロニトリルを水和して得られるアクリルアミドを使用して、凝集性能や溶解性の優れた高性能のアクリルアミド系重合体を製造する方法に関するものである。

アクリルアミド系重合体は、その優れた性能によつて、凝集剤、増粘剤、製紙工業における紙力

増強剤、伊水性向上剤、その他数多くの用途を有する有用な重合体である。

従来の技術

従来、工業的に得られるアクリルアミドは、そのほとんど全てが銅含有触媒を用いてアクリロニトリルを水和する所謂接触水和法により製造されたものである。従つて、従来のアクリルアミド系重合体は、これら接触水和法により得られたアクリルアミドを原料とするものに限定されていた。しかしながら、上記接触水和法においては、得られたアクリルアミド水溶液中に反応副生物や触媒に由来する微量の不純物が混入し、これを精製工程によつて完全に取り除くことが難しく、アクリルアミド系重合体の用途によつてはその原料として必ずしも満足し得るものではなかつた。

一方、最近、本出願人らによりニトリル水和能を有する微生物を利用したアクリロニトリルからのアクリルアミドの製造法が提案されている(特公昭56-17918号、同56-38118号および同57-1234号公報参照)。この方法によれば、凝

炭素反応に特徴的である高選択性によりアクリルアミド以外の副生物がほとんど生成しないことおよび触媒である微生物菌体からの不純物の溶出が極めて少ないため、得られたアクリルアミド水溶液は通常そのまま各種重合体製造用の原料として使用することが可能である。

#### 発明が解決しようとする問題点

本発明は、このような微生物反応により得られるアクリルアミド水溶液の利点を最大限活用し、さらに高分子量で溶解性の良い高性能のアクリルアミド系重合体を得ようとするものである。一般に、高分子量になる程溶解性は低下する傾向にあるが、触媒剤や製紙工業における抄紙用粘剤等の用途においては、高分子量で且つ溶解性の優れていることが特に要求される。

#### 問題点を解決するための手段

本発明は、上記のごとき高性能のアクリルアミド系重合体を得るべく種々検討した結果、微生物反応により得られたアクリルアミド水溶液を活性炭処理し、これを重合に供することが極めて効果

的であることを見出しなされたものである。

すなわち、本発明は、ニトリル水と能を有する微生物の作用により水性媒体中でアクリロニトリルを水和して得られるアクリルアミド水溶液を活性炭で処理し、このアクリルアミド水溶液またはこれを主体とする単液混合物を重合することを特徴とするアクリルアミド系重合体の製造方法を要旨とするものである。

#### 微生物：

本発明で使用する微生物はアクリロニトリルを水和してアクリルアミドを生成する能力のある微生物であり、具体的に例えば、前記特公昭56-17918号公報等に記載されているコリネバクテリウム (*Corynebacterium*) 属のN-771菌株 (微工研菌寄第4445号) およびN-774菌株 (微工研菌寄第4446号) ならびにノカルジア (*Nocardia*) 属のN-775菌株 (微工研菌寄第4447号)、その他特開昭51-86186号公報記載のバチルス (*Bacillus*) 属、バクテリジウム (*Bacteridium*) 属、マイクロコカス

(*Micrococcus*) 属およびブレヴィバクテリウム (*Brevibacterium*) 属の各菌株および特公昭59-37951号公報記載のシュードモナス (*Pseudomonas*) 属の菌株等が挙げられる。

#### 水和反応：

本発明の水和反応を実施するに当つては、前記した微生物の一種を選び、例えば、前記特公昭56-17918号、同56-38118号公報等に記載された方法に準じて培養し、その培養液、培養液から分離した菌体、または菌体処理物 (粗酵素、固定化菌体等) を水、生理食塩水または緩衝液に溶解し、これにアクリロニトリルを共存せればよい。上記反応条件としては、通常、懸濁液中の微生物菌体濃度：1~10重畳またはアクリロニトリル濃度：0.5~1.0重畳、pH：7~9、温度：水点~15℃、時間：0.5~1.0時間である。また、反応は回分、半回分連続のいずれでもよいが、基質であるアクリロニトリルは本酵素反応に対する阻害作用が大きいため、系内の基質濃度は2重畳以下になるように調整しつつ反応を

行うのが好ましい。かくして、収率100%の转化率でアクリルアミドを生成させることができる。活性炭処理：

本発明で使用する活性炭は特殊なものではなく、通常の市販のものでよく、その形状は粒状、粉末状を問はない。これらの活性炭は木材、果実殻、石灰、石油残査等を原料とするものであり、賦活法としてガス賦活、薬品賦活が行われているものである。

これらの活性炭によるアクリルアミド水溶液の処理は、該水溶液中に活性炭を添加、攪拌すること、あるいは該水溶液を活性炭を充填した層に供給、流出させることによつて行われる。これらの操作は回分、連続いずれでもよい。

活性炭の使用量はアクリルアミドに対し0.05~3重畳、好ましくは0.1~1重畳であり、0.05重畳未満では充分効果が得られない。3重畳を超えると経済的に問題となるだけでそれ以上の効果は得られない。

処理温度は、通常水和反応終了後の反応液の温

成(氷点-15℃)から常温程度であり特に限定されない。

また、アクリルアミド水溶液と活性炭との接触時間は通常約1時間以内で充分である。

得られた精製アクリルアミド水溶液は、必要によりろ過、濃縮を行い重合に供せられる。

重合:

本発明のアクリルアミド系重合体は、このようにして得られたアクリルアミド水溶液をそのまま、あるいは、これにアクリルアミドと共重合可能な他のビニル単量体、例えばアクリル酸またはその塩、メタクリルアミド、2-アクリルアミド-2-メチルプロパンスルホン酸またはその塩、ジメチルアミノエチルメタクリレートまたはその四級塩等を通常50重量%以下融合し重合することによつて得られる。また、最終的に得られる重合体の水溶性を損なわない範囲の量でアクリル酸低級アルキルエステル、メタクリル酸メチル、アクリロニトリル、スチレン等を共重合してもよい。

単量体の濃度は通常5~40重量、好ましくは

合を開始することができる。

以下、実施例によつて本発明を具体的に説明する。

#### 実施例

アクリルアミド水溶液の製造:

##### 製造例1

コリネバクテリウム属N-774菌株(微工研寄第4446号)を培養して得た微生物菌体をアクリルアミド/メチレンビスアクリルアミド=95/5(重量比)40重量%の水溶液中に8重量%の腐敗となるように懸濁させ、これにアンモニウムパーオキシドおよびトリエタノールアミンを加えて5~30℃で約1時間重合して、ゲル化した固定化菌体とした。

この固定化菌体を0.5%濃に成形した後、これをゲル濃度が0.5重量%となるようにアクリロニトリル20重量%の水溶液中に攪拌懸濁させて、苛性ソーダによりpH8.5に調整した。次いで、この懸濁液の濃度を0℃に保ちながらアクリロニトリル13.0重量%を反応系中の濃度が2重量%を

10~30重量%となるように調整する。

重合温度は0~100℃の範囲で適宜選択されるが、通常の重合槽を使用する重合の場合、重合熱による系内の温度上昇および高分子量の重合体を得ることを考慮して、重合開始温度は10~30℃程度とすることが好ましい。

重合開始剤としては、通常使用されるラジカル開始剤、例えば、過硫酸塩、過塩素酸塩、過酸化水素、過酢酸塩、クメンハイドロパーオキシド、ターシヤリブチルハイドロパーオキシド等の酸化性物質、またはこれらの酸化性物質とアミン化合物、還元性スルホキシ化合物、アスコルビン酸、レニウ酸、ロンガリット等との組合せによるレッドブクス系開始剤、あるいはさらにアゾビスイソプロピロニトリル、アゾビスアミノプロパン塩酸塩、アゾビスエタノールニトリル、2,2'-アゾビス(メトキシエタノール)ニトリル、2,2'-アゾビス(メトキシエタノール)ニトリル等のアゾ化合物、またはこれと前記酸化性物質やレッドブクス系開始剤を組合せた系が挙げられる。

また、上記以外に光や放射線照射によつても重

組えないように連続的に液加し、全体で約20時間反応を行い、反応後固定化菌体を分離しアクリルアミド濃度20重量%の水溶液を得た。

##### 製造例2

製造例1で得たアクリルアミド水溶液5%を減圧下に40℃に加熱し濃縮し約3時間でアクリルアミド濃度41.0重量%の水溶液を得た。

##### 製造例3

製造例1で得たアクリルアミド水溶液にアクリルアミドに対して0.5重量%の粉末活性炭(白炭A武田薬品工業製)を用いて攪拌下、空気を吹き込みながら室温で1時間処理した。処理液は製造例2と同様に濃縮してアクリルアミド濃度40.5重量%の水溶液を得た。

##### 製造例4

製造例1で得たアクリルアミド水溶液をアクリルアミドに対して0.3重量%となるように粒状活性炭(KLH250武田薬品工業製)を充ちた固定層を用いて室温で連続的に処理した。処理液は製造例2と同様に濃縮してアクリルアミド濃度

表 - 1

| 品    | アクリルアミド水溶液 | 1%粘度<br>(cps) | 溶解性<br>(%) |
|------|------------|---------------|------------|
| 実施例1 | 製造例3       | 2580          | 0          |
| # 2  | # 4        | 2580          | 0          |
| 比較例1 | # 2        | 2400          | 0          |
| # 2  | 市販品        | 2570          | 2          |

1%粘度：1%重合体水溶液に2NH<sub>4</sub>SO<sub>4</sub>を加えてpHを2.5に調整し25℃でB型粘度計を用いて測定した。

溶解性：0.1%重合体水溶液1000φを調整し、これを80メッシュの篩を過し器上に残ったゲルの重量を測定した。

以下、同様

実施例3、4および比較例3、4

先の実施例および比較例と同様にして得た5mm角の解凍ゲルのそれぞれに低ゲル中に含まれるアクリルアミドの10モル%に相当する濃度30重量%の苛性ソーダ水溶液を混合し、60℃で20

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以下、同様

実施例5、6および比較例5、6

実施例1、2および比較例1、2と同じアクリルアミド水溶液を用い、ホウ酸0.8重量%、苛性ソーダ $\xrightarrow{1.2}$ 重量%を含有するアクリルアミド濃度2.80重量%の水溶液を調整し、デュワー瓶に仕込んだ。次いで、11℃に保ちながら窒素ガスを吹込んで水溶液中および容器内の空気を窒素置換したのち、開始剤として過硫酸カリウム30ppmおよびジメチルアミノプロピオニトリル650ppmを添加した。約15分の誘導時間後、重合は急激に進行して約100分後に最高温度94℃に達した。以下、実施例1、2および比較例1、2と同様にして図-3の結果を得た。

4.2.2 炭酸ナトリウム水溶液を得た。

実施例1、2および比較例1、2

製造例3、4、および比較例として製造例2のアクリルアミド水溶液ならびに市販アクリルアミド水溶液(濃度50重量%、金鋼系触媒法)をアクリルアミド濃度2.60重量%、pH7.0に調整し、デュワー瓶に仕込んだ。次いで、15℃に保ちながら窒素ガスを吹き込んで水溶液中および容器内の空気を十分に窒素置換したのち、開始剤としてアゾビス(2-ナフタレン)酸100ppm、過硫酸カリウム30ppmおよびジメチルアミノプロピオニトリル450ppmを添加した。約15分の誘導時間の後に重合は急激に進行し、約70分後には最高温度92℃に達した。そのまま約1時間放置後ゲル状の内容物を取り出し、5mm角に解凍し60℃で16時間熱風乾燥した。乾燥品(重合体)をクレーン粉砕機で2mm以下に粉砕し、その1%水溶液の粘度、溶解性および凝集性能を測定し結果を表-1に示した。

時間放置後、60℃で16時間熱風乾燥した。以下、先の実施例および比較例と同様の操作を行い図-2の結果を得た。

表 - 2

| 品    | アクリルアミド水溶液 | 1%粘度<br>(cps) | 溶解性<br>(%) | 凝集性能 |
|------|------------|---------------|------------|------|
| 実施例3 | 製造例3       | 1920          | 0          | ○    |
| # 4  | # 4        | 1800          | 0          | ○    |
| 比較例3 | # 2        | 1650          | 0          | ○    |
| # 4  | 市販品        | 1730          | 5          | ○    |

凝集性能：内径35mm、長さ350mmの沈降管にカオリン(土庫カオリンA-38)の5%懸濁液100ml(pH7)を投入し、0.1%重合体水溶液5mlを加え10回転倒し、転倒終了後沈降界面が液全体の容積の1/2になるまでに要する時間を測定した。向この時間は重合体の粘度によつて絶対値が異なるので相対的に効率の比較を行った(○良好、△

表 - 3

| 点    | アクリルアミド水溶液 | 1多粘度<br>[cps] | 溶解性<br>[φ] | 凝集性能 |
|------|------------|---------------|------------|------|
| 実施例5 | 製造例3       | 1380          | 4          | ○    |
| #6   | #4         | 1320          | 3          | ○    |
| 比較例5 | #2         | 1180          | 3          | △    |
| #6   | 市販品        | 1280          | 7          | ○    |

実施例7、8および比較例7、8

実施例1、2および比較例1、2と同じアクリルアミド水溶液を用い、アクリルアミド1.9.2重量多および2-アクリルアミド-2-メチルプロパンスルホン酸4.8重量多、pH7の水溶液を調製し、デュワー瓶に仕込んだ。系内の空気を窒素置換後、開始剤としてアゾビスシアノヴアレリン酸100ppm、アゾビスアミノプロパン塩酸塩300ppm、過硫酸カリウム5ppmおよびジメチルアミノプロピオニトリル250ppmを添加した。約20分の誘導時間の後に重合は急激に進行して約100分後に最高温度80℃に達した。以下、先

温度85℃に達した。以下、先の例と同様にして表-5の結果を得た。

表 - 5

| 点    | アクリルアミド水溶液 | 1多粘度<br>(NaCl)<br>[cps] | 溶解性<br>[φ] | 凝集性能 |
|------|------------|-------------------------|------------|------|
| 実施例9 | 製造例3       | 2150                    | 2          | ○    |
| #10  | #4         | 2050                    | 2          | ○    |
| 比較例9 | #2         | 1850                    | 2          | △    |
| #10  | 市販品        | 2050                    | 48         | △    |

1多粘度(NaCl): 1多重合体水溶液の粘度を1/5NaCl水溶液中、25℃でB型粘度計を用い測定した。

凝集性能: カオリンの5多懸濁液(pH7)の代りに顔料ウルトラマリンブルー(第一化成工業製品) #1200の2多懸濁液を用いた他は表-2と同様に評価を行った。

特許出願人

日北化学工業株式会社

の例と同様に表-4の結果を得た。


表 - 4

| 点    | アクリルアミド水溶液 | 1多粘度<br>[cps] | 溶解性<br>[φ] | 凝集性能 |
|------|------------|---------------|------------|------|
| 実施例7 | 製造例3       | 3410          | 5          | ○    |
| #8   | #4         | 3400          | 3          | ○    |
| 比較例7 | #2         | 3000          | 3          | ○    |
| #8   | 市販品        | 3200          | 20         | ○    |

実施例9、10および比較例9、10

実施例1、2および比較例1、2と同じアクリルアミド水溶液を用い、アクリルアミド2.0.5.7重量多およびジメチルアミノエチルメタクリレート1.4.3重量多、pH3.5の水溶液を調製し、デュワー瓶に仕込んだ。系内の空気を十分に窒素置換した後、開始剤としてアゾビスイソプロパロニトリル400ppm、アゾビスアミノプロパン塩酸塩600ppm、過硫酸アンモニウム2ppmおよびロンガリット6ppmを添加した。約10分の誘導時間の後に重合は急激に進行し約120分後に最高

**PURIFICATION OF AQUEOUS SOLUTION OF UNSATURATED AMIDE**

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Applicant(s):: NITTO CHEM IND CO LTD  
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**Abstract**

**PURPOSE:**To remove various impurities from an aqueous solution of an unsaturated amide produced by the hydration of an unsaturated nitrile, without causing the troubles such as polymerization, etc., in high efficiency, by using an ion exchange membrane.

**CONSTITUTION:**The objective material can be prepared by removing organic acids, inorganic salts and organic salts from an aqueous solution of an unsaturated amide prepared by the hydration of the corresponding unsaturated nitrile such as acrylonitrile, methacrylonitrile, etc., by using an electro dialysis apparatus furnished with an ion exchange membrane, at 5-10pH, preferably 6-8pH at 0-50 deg.C. If necessary, the product is further purified with ion exchange resin, activated carbon, etc. The unsaturated amide, especially acrylamide, methacrylamide, etc. is useful as a raw material of polymers for flocculant, thickener, petroleum-recovering agent, soil-improver, paper strengthening agent for paper-making industry, thickening agent for paper making, etc.

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⑮ 発明の名称 不飽和アミド水溶液の精製方法

⑯ 特 願 昭59-235107

⑰ 出 願 昭59(1984)11月9日

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# 明 細 書

## 1. 発明の名称

不飽和アミド水溶液の精製方法

## 2. 特許請求の範囲

(1) イオン交換膜を用いることを特徴とする不飽和ニトリルを水と和して得られる対応する不飽和アミド水溶液の精製方法。

(2) 不飽和ニトリルがアクリロニトリルまたはメタクリロニトリルである特許請求の範囲第1項記載の精製方法。

## 3. 発明の詳細な説明

### 産業上の利用分野

本発明は、不飽和ニトリルを水と和して得られる対応する不飽和アミド水溶液の精製方法に関する。不飽和アミド、特にアクリルアミド、メタクリルアミド等は凝集剤、増粘剤、石油回収薬剤、土壌改良剤、製紙工業における低力増強剤、抄紙用粘剤および浮水性上剤等数多くの用途を有する重合体の原料として極めて有用な物質である。

### 従来の技術

アクリルアミド、メタクリルアミド等の不飽和アミドは対応する不飽和ニトリルを水性媒体中でフナー銅、還元銅、銅クロム、銅亜鉛等の金属銅系触媒に接触、水和して製造する方法が広く知られている。また、最近では、ニトリル水和能を有する微生物を利用して、不飽和ニトリルを水と和して対応する不飽和アミドを製造する方法が提案されている。

これら不飽和アミドの製造法の中、特に金属銅系触媒を用いる場合は、一般に反応温度が60～150℃、反応圧力が0～20 kg/cm<sup>2</sup>と高いため副反応が起こり易く、これらの副生物(有機酸等)や触媒に由来する金属イオン等の不純物を得られたアミド水溶液中から除去する精製操作が必須である。特に、前記したような重合体の原料として用いるためには、重合に悪影響を及ぼすような不純物は極力除去することが必要である。

微生物を利用する場合、反応が常態、常圧で行なわれるため、金属銅系触媒使用の場合に比べて生成アミド水溶液中には無機塩類、反応副生物



や微生物菌体からの抽出物等の不純物は極めて少ないが、これらの無機塩類も高性能のアミド重合体の製造を目的とする場合には除去することが好ましい。

これらアミド水溶液中の不純物を除去する方法として、蒸留、抽出、晶析等が考えられるが、これらの方法は何らかの形で加熱操作が必要であり、一般に熱に対して不安定な不飽和アミドの精製法としては適当でない。

工業的に実用化されている不純物を除去するための方法としてはイオン交換樹脂を用いる方法がある。この方法は、極めて微量の有機酸や無機塩を除去するには効果的であるが、これらの不純物が不飽和アミドに対して数々のオーターにもなるとイオン交換樹脂が多量に必要となるだけでなく、再生頻度が高くなり、コストが増大し、また樹脂附近での重合トラブルも生じ易い。

イオン交換樹脂は大きく分けてカチオン交換樹脂とアニオン交換樹脂があり、本発明のような有機酸や無機塩等の不純物を含む場合には当然上記

2種類の樹脂が必要となる。樹脂に物質が吸着するときの適正pHはカチオン樹脂とアニオン樹脂とは当然異ってくるし、従つて、pHによる吸着の度合いについても考慮しなければならない。さらに、本発明のような不飽和アミドを取扱う場合には重合トラブルにも注意が必要である。すなわち、不飽和アミド類はその水溶液は理由がよく分らないが、pHが低い場合（特にpH 5以下）イオン交換樹脂附近で重合を起こすことが非常に多い。

さらにまた、不飽和有機酸を除去する方法としては、その水溶液をアルカリで中和して逆浸透膜で分離する方法が提案されている（特開昭56-92254号公報参照）。この方法は、アミドと水は逆浸透膜を通過させて、有機酸は通過せずに両者を分離しようとするものであるが、同程度の分子量の樹脂の場合、例えば、アクリルアミドとアクリル酸のような場合にはほとんど分子量が同一であり、きれいに分離することはなかなか困難である。

#### 発明が解決しようとする問題点

本発明は、不飽和ニトリルを水和して得られる対応する不飽和アミド水溶液中の各種不純物を重合等のトラブルを生ずることなく効率よく除去し、各種重合体製造原料等として通した不飽和アミド水溶液を得ようとするものである。

本発明で除去の対象となる不飽和アミド水溶液中の不純物は不飽和アミドの製造条件にもよるが、有機酸、例えばアクリルアミド製造の際に副生するアクリル酸、および微生物の培養、固定化菌体の培養、ニトリル水和反応等の際に用いる各種添加剤に由来する $KCl$ 、 $NaCl$ 、 $K_2SO_4$ 、 $Na_2SO_4$ 、 $K_2CO_3$ 、 $Na_2CO_3$ 、 $(NH_4)_2CO_3$ 、 $NH_4Cl$ 、 $(CH_3)_2SO_4$ 、 $CaCl_2$ 、 $CaSO_4$ 、 $KNO_3$ 、 $NaNO_3$ 、 $NH_4NO_3$ 、 $Ca(NO_3)_2$ 、 $K_2PO_4$ 、 $Na_2PO_4$ 、 $K_2HPO_4$ 、 $Na_2HPO_4$ 、 $KH_2PO_4$ 、 $NaHSiO_3$ 、 $K_2SiO_3$ 、 $Na_2SiO_3$ 、 $CaSiO_3$ 、 $NH_4I$ 、 $KI$ 、 $NaI$ 、 $Na_2BO_3$ 、 $(NH_4)_2CrO_4$ 、 $K_2CrO_4$ 、 $Na_2CrO_4$ 、 $10H_2O$ 、 $(NH_4)_2CO_3$ 等の無機塩や $(COONH_2) \cdot H_2O$ 、 $(COOK) \cdot H_2O$ 、 $C_6H_5CO_2Na \cdot H_2O$ 、 $(C_6H_5CO_2)_2Ca \cdot 3H_2O$ 、 $C_6H_5SO_3Na$ 等の有機塩等である。

#### 問題点を解決するための手段

本発明は、上記のごとき問題点を解決すべく鋭意検討した結果、種々の不純物を含む不飽和アミド水溶液の精製に、イオン交換膜の使用が極めて有効であることを見出しなされたものである。

すなわち、本発明は、イオン交換膜を用いることを特徴とする不飽和ニトリルを水和して得られる対応する不飽和アミド水溶液の精製方法を要旨とするものである。

本発明によれば、一定のpH領域で、しかも中性付近のpHで電気的に中性である不飽和アミドと電解質である有機酸や無機塩類、有機塩類等を効率的に除去することが可能である。

本発明のイオン交換膜を用いる方法が、イオン交換樹脂法と異なる点は、不純物の種類によつてpHを調整する必要がなく重合等のトラブルを生じないこと、さらに、かなり高濃度の不純物でも処理できること、また、逆浸透膜法と異なる点は、膜を通過する物質が電解質であり、同程度の分子量のものでも一方が電解質であれば両者は分離が

可能であることである。

本発明においては、除去の対象となる不純物はイオン解離してイオン交換膜を通過するものであり、従つて、除去しようとする物質の解離定数とも関連するが、通常 pH は 5 ~ 10、好ましくは 5 ~ 8 の範囲である。

また、イオン交換膜を用いる際の流速は特に制限されるものではないが、不飽和アミドの場合および膜処理での液の抵抗等を考慮すると通常 0 ~ 50 セの範囲とするのが好ましい。

また、本発明における不飽和アミド水溶液の濃度についても特に制限されるものではなく、通常の不飽和アミドの製造濃度数%以上から、これを濃縮して得られる濃度 40 ~ 50 重量%程度に至るまで処理することができるとする。

さらに、不飽和アミド水溶液中に含まれる不純物についても通常数 ppm から数 10 % に至る濃度で処理可能である。

本発明で使用するイオン交換膜を装備した装置としては、例えば海水の濃縮等に用いられるもので

特殊な装置である必要はない。通常はカチオン交換膜とアニオン交換膜が交互に並べられ、その両端に直流電圧が与えられるようになっていて所謂電気透析装置であればどのような形式のものであつてもよい。このような装置を使用することにより、原液中のイオン性物質は両端のカソードまたはアノードに引かれて膜を通過し、結果として非イオン物質のみがそのまま原液中に残ることとなる。

このように、本発明によれば非イオン物質である不飽和アミド水溶液から不飽和有機酸、無機および有機塩類を除去することができるが、さらにこれらの処理に加えて必要に応じてイオン交換樹脂や活性炭等に処理を行つてもよい。

次に、実施例によつて本発明をさらに具体的に説明する。

#### 実施例 1

##### 実施例 1

アクリルアミド 19.8 重量%、アクリル酸 334 ppm、NaCl 800 ppm を含む水溶液を苛性ソー

ダを用いて pH 7.0 に調整し、液温 25℃ で旭ガク（社）製の実験用電気透析装置 Du-ob 型の原液側にセットした。この装置の透過液側には蒸留水をセットして、各々 4.8 L/hr の速度で装置を通して循環させながら直流電圧（10V）を加えた。約 5 時間後の原液の分析値はアクリルアミド 18.7 重量%、アクリル酸 39.3 ppm、NaCl 35 ppm であり、重合物は全く検出されなかった。

#### 実施例 2

アクリルアミド 34.0 重量%、アクリル酸 632 ppm、NaCl 1400 ppm を含む水溶液について、実施例 1 と同様の操作を行つた。その結果、約 5 時間後の原液の分析値はアクリルアミド 33.9 重量%、アクリル酸 54.6 ppm、NaCl 40 ppm であり、重合物は全く検出されなかった。

特許出願人

日東化学工業株式会社

昭 62. 9. 14 発行

手 続 補 正 書

昭和62年5月29日

特許法第17条の2の規定による補正の掲載

昭和59年特許願第235107号(特開昭  
61-115058号, 昭和61年6月2日  
発行 公開特許公報 61-1151号掲載)につ  
いては特許法第17条の2の規定による補正があっ  
たので下記のとおり掲載する。 3 ( 2 )

特許庁長官 黒田明雄殿

| Int. Cl. 4            | 識別記号 | 庁内整理番号             |
|-----------------------|------|--------------------|
| C07C103/133<br>102/08 |      | 8519-4H<br>8519-4H |

## 1. 事件の表示

昭和59年特許願第235107号

## 2. 発明の名称

不飽和アミド水溶液の精製方法

## 3. 補正をする者

事件との関係 特許出願人

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## 4. 補正の対象

明細書の発明の詳細な説明の欄

## 5. 補正の内容

明細書第1頁第16～17行の「土壌改良剤」を

「土壌改良剤」に訂正します。

方式  
審査

（押印）



13



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57 Designated Contracting States: DE FR GB

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58 Method for purifying aqueous acrylamide solution.

75 A method for purifying an aqueous acrylamide solution by using activated carbon is disclosed. The method comprises contacting activated carbon with water having oxygen dissolved therein until the dissolved oxygen concentration in water after the contact increases to at least 0.5 ppm, and then contacting the aqueous acrylamide solution with the thus treated activated carbon. The method can prevent polymerization of acrylamide around activated carbon, and the resulting purified aqueous acrylamide solution requires no further purification, such as ion-exchanging.

EP 0 182 578 A1

## METHOD FOR PURIFYING AQUEOUS ACRYLAMIDE SOLUTION

FIELD OF THE INVENTION

This invention relates to a method for purifying an aqueous acrylamide solution, and more particularly to a method for purifying an aqueous acrylamide solution with activated carbon that has  
5 been subjected to a specific treatment.

BACKGROUND OF THE INVENTION

Acrylamide has hitherto been prepared by a so-called catalytic hydration process which comprises reacting acrylonitrile with water in the presence of a  
10 catalyst, such as a copper catalyst.

An aqueous acrylamide solution prepared by the catalytic hydration process tends to undergo coloration or become turbid immediately after the  
15 preparation thereof, or with the passage of time, due to trace amounts of impurities, such as decomposition products of a stabilizer present in the starting acrylonitrile, substances eluted from the catalyst used, by-products, and the like.

20 The crude aqueous acrylamide solution containing such impurities should be subjected to a purification step to remove the color or turbidity before it is commercially presented in the form of an aqueous solution or crystals. It has been generally considered

preferable to carry the purification by passing the aqueous solution through a column packed with activated carbon, particularly granular activated carbon. However, acrylamide is very apt to be polymerized around activated carbon, thus causing obstruction of the column. As a result, the advantages of the granular activated carbon cannot be fully utilized. In an attempt to prevent polymerization of acrylamide, a method has been proposed of incorporating cupric ion in the activated carbon in advance, as disclosed in Japanese Patent Publication No. 28608/76 (corresponding to U.S. Patent 3,923,741).

In recent years, a process for preparing acrylamide by direct hydration of acrylonitrile using microorganisms capable of hydrating nitriles has been proposed, as described, e.g., in Japanese Patent Application (OPI) No. 86186/76 (corresponding to U.S. Patent 4,001,081) and Japanese Patent Publication No. 17918/81 (corresponding to U.S. Patent 4,248,968) (the term "OPI" used herein means an "unexamined published application"). According to this microbiological process, if the acrylamide concentration is increased, pigments and traces of impurities tend to be extracted from the microorganism to enter into the aqueous solution. Therefore, it is desirable to purify the aqueous solution obtained by this process by treating

with activated carbon similarly as in the case of the aforesaid catalytic hydration process.

However, when the acrylamide aqueous solution obtained by the microbiological process is purified using activated carbon in which cupric ion has been incorporated for the purpose of preventing polymerization of acrylamide in accordance with the conventional technique, the cupric ion tends to be extracted into the aqueous solution, resulting in not only reduction of cupric ions adsorbed on the activated carbon to readily cause polymerization of acrylamide around the activated carbon, but also incorporation of cupric ions that were not formerly present in the crude aqueous solution in the purified solution. The extraction or dissolution of cupric ions in the acrylamide aqueous solution is believed related to a copper ion equilibrium between activated carbon and the aqueous solution. An aqueous acrylamide solution containing a cupric ion even in a trace amount is unsuitable as a monomer for obtaining high molecular weight polymers, and is, therefore, required to be further purified by ion-exchange resins.

#### SUMMARY OF THE INVENTION

Accordingly, an object of this invention is to provide a method of purifying an aqueous acrylamide solution by using activated carbon, which can prevent

polymerization of acrylamide around activated carbon without requiring any further purification procedure with ion-exchange resins.

Thus, the present invention is directed to a  
5 method for purifying an aqueous acrylamide solution by using activated carbon, which comprises contacting activated carbon with water having oxygen dissolved therein until the dissolved oxygen concentration in the  
effluent water that has been contacted with the activated  
10 carbon increases to at least 0.5 ppm, and then contacting the aqueous acrylamide solution with the thus treated activated carbon.

#### DETAILED DESCRIPTION OF THE INVENTION

In the present invention, it is necessary to  
15 contact the activated carbon to be used with water containing dissolved oxygen until the resulting water after contact has a dissolved oxygen concentration of not less than 0.5 ppm, and preferably not less than 1 ppm.

Contact between activated carbon and water containing dissolved oxygen can usually be carried out  
20 by passing water containing dissolved oxygen through a packed bed, e.g., a column, packed with activated carbon. In this case, after the concentration of dissolved oxygen in the effluent water reaches at least 0.5 ppm, an  
aqueous acrylamide solution can be fed to the activated  
25 carbon-packed bed.



Water to be fed to activated carbon should have a dissolved oxygen concentration of at least 1 ppm, and preferably 3 ppm or more. When water having a high dissolved oxygen concentration is fed to activated carbon, the dissolved oxygen concentration in the effluent water initially falls to 0.1 ppm or less, but then gradually rises as feeding is continued for a long time, usually for 1 hour to 5 days.

Water is usually fed to activated carbon at a space velocity of from 0.1 to 20 l/hr. Since it takes a long time for the dissolved oxygen concentration in the effluent to rise, the quantity of water to be used may be reduced by providing an oxygenating device and circulating water through activated carbon and the oxygenating device whereby oxygen is dissolved in water circulated from the activated carbon, and the water thus having an increased dissolved oxygen concentration is fed back to the activated carbon. In the oxygenating device, water is brought into contact with air or oxygen in order to absorb oxygen. Oxygen absorption (oxygenation) can be achieved by means of a generally employed device, or may be performed in a piping capable of contacting water with air or oxygen or within an apparatus for treating an aqueous acrylamide solution with activated carbon.

In the case of using pure water, which usually has a reduced dissolved oxygen concentration as low as 0.5 ppm after having been passed through a decarbonater, it should be contacted with air or oxygen in an oxygenating device so as to have an increased dissolved oxygen concentration.

The present invention is mainly applied to a fixed bed using granular activated carbon and may also be applicable to a fluidized bed using granular activated carbon. The present invention may further be applied to powdery activated carbon used in a fixed bed or other similar systems.

The present invention is suitable for purification of an aqueous acrylamide solution which does not contain a polymerization inhibitor, e.g., a copper ion, etc., and, in particular, an aqueous acrylamide solution obtained by a microbiological process. The present invention may also be applied to an aqueous acrylamide solution containing a cupric ion that is obtained by a catalytic hydration process. In this case, since there is no need to previously adsorb a copper ion onto activated carbon, the copper ion in the purified aqueous acrylamide solution can be reduced according to the method of the present invention.

According to the present invention, a purified aqueous acrylamide solution can be stably obtained while preventing incorporation of a polymer due to polymerization of acrylamide around activated carbon by contacting a crude aqueous acrylamide solution with activated carbon which has been contacted with water having a high concentration of dissolved oxygen.

When the present invention is applied to an aqueous acrylamide solution obtained by a microbiological process, the resulting purified acrylamide can be subjected to polymerization without any further treatment for removing copper ions, such as ion-exchanging, but replacement of oxygen in a polymerization system with nitrogen that is usually conducted before polymerization, to thereby produce an extremely high molecular weight polyacrylamide useful as a coagulant, etc. To the contrary, the conventional purification method involves adsorption of copper ions onto activated carbon prior to treatment, and thus requires removal of copper ions eluted out during the treatment from the treated aqueous acrylamide solution by, for example, ion-exchanging.

Further, the reducing property and oxygen adsorptivity of activated carbon vary depending on the kind thereof. According to the present invention,

an aqueous acrylamide solution is fed to activated carbon after the activated carbon is treated with water having a high dissolved oxygen concentration until the dissolved oxygen concentration of the effluent water is increased to at least a desired predetermined level. Therefore, the dissolved oxygen concentration of the aqueous acrylamide solution passing through the activated carbon-packed bed can be maintained constant at said predetermined level or higher, and the acrylamide can be prevented from polymerization irrespective of the kind of activated carbon used.

The present invention is now illustrated in greater detail with reference to the following example. In the examples, all the parts and percents are by weight unless otherwise indicated.

#### EXAMPLE 1

A microorganism belonging to the genus Corynebacterium and capable of hydrating a nitrile, N-774 strain (FERM-P No. 4446), was aerobically cultivated in a medium (pH 7.2) containing 1% of glucose, 0.5% of peptone, 0.3% of yeast extract, 0.3% of malt extract and 0.05% of ferric sulfate heptahydrate. Forty parts of washed microbial cells collected from the culture (water content: 75%), 45 parts of

acrylamide, 0.5 part of N,N'-methylenebisacrylamide and 40 parts of a 0.05M phosphoric acid buffer (pH 7.7) were mixed to form a uniform suspension... To the suspension were added 5 parts of a 5% aqueous solution of

5 dimethylaminopropionitrile and 10 parts of a 2.5% potassium persulfate aqueous solution, and the resulting mixture was maintained at 10°C for 30 minutes to effect polymerization. The resulting massive gel containing the microbial cells was crushed to small particles and

10 thoroughly washed with a 0.05M phosphoric acid buffer (pH 7.7) to obtain 100 parts of the immobilized microbial cells.

Water and acrylonitrile were reacted at 0°C in the presence of the above prepared immobilized

15 microbial cells in a continuous reactor equipped with a stirrer to obtain a 20% aqueous solution of acrylamide.. The resulting aqueous solution was found to contain 100 ppm of the unreacted acrylonitrile and not more than 0.02 ppm of a copper ion and have a chromaticity of

20 about 6 APHA.

Separately, a glass-made column having an inner diameter of 60 mm and a length of 2 m was packed with 1,500 g of granular activated carbon ("Granular Shirasagi W 5C", a trade mark of product manufactured

25 by Takeda Chemical Industries, Ltd.). A 1 liter-volume

At

agitator and the column were connected by piping, and water was circulated therethrough at a rate of 8 l/hr by means of a pump, simultaneously with blowing air into the agitator. The dissolved oxygen concentration in the water running into the column was not less than 6 ppm, but that in the water effused from the column was not more than 0.1 ppm after ten hours from the start of circulation. Fifty-eight hours after the start of circulation, the dissolved oxygen concentration in the effluent had increased to 3 ppm.

At this point of time, the 20% aqueous solution of acrylamide as above obtained was passed through the column packed with activated carbon at a rate of 8 l/hr and discharged out of the system. The temperature of the aqueous solution was not higher than 10°C. When the aqueous acrylamide solution was fed over 12 days, the effluent had a chromaticity of about 1 APHA, and a polymer was noted in neither the column nor the effluent.

Confirmation of a polymer in the effluent was conducted by adding 100 ml of methanol to 10 ml of an effluent sample and examining whether white turbidity appeared.

COMPARATIVE EXAMPLE 1

The same procedures as described in Example 1 were repeated except that water having a dissolved oxygen concentration of 6 ppm or more was circulated for 16 hours (the dissolved oxygen concentration in the effluent water increased to 0.3 ppm) and at this point the aqueous acrylamide solution was fed to the column packed with activated carbon.

The effluent after 1 or 2 days from the start of the feeding was free from formation of a polymer, but that after 3 days became turbid immediately upon addition of methanol, indicating the presence of a polymer. Formation of a number of popcorn-shaped polymer particles was noted in the interior of the column of activated carbon, with a solution polymer being adhered to a part of said popcorn-shaped polymer particles.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

## CLAIMS:

1. A method for purifying an aqueous acryl-  
amide solution by using activated carbon, which  
comprises contacting activated carbon with water having  
oxygen dissolved therein until the dissolved oxygen  
concentration in the effluent water that has been  
5 contacted with the activated carbon increases to at  
least 0.5 ppm, and then contacting the aqueous acryl-  
amide solution with the thus treated activated carbon.
2. A method as in claim 1, wherein the  
contacting between the activated carbon and water  
having oxygen dissolved therein is carried out by  
passing the water through a packed bed of activated  
5 carbon.
3. A method as in claim 1, wherein said water  
having oxygen dissolved therein has a dissolved oxygen  
concentration of at least 1 ppm.
4. A method as in claim 3, wherein said water  
having oxygen dissolved therein has a dissolved oxygen  
concentration of at least 3 ppm.
5. A method as in claim 2, wherein the  
effluent water that has been contacted with the acti-  
vated carbon is passed through an oxygenating device  
wherein additional oxygen is dissolved in the water  
and the water having the thus increased dissolved



oxygen concentration is contacted with the activated carbon.

6. A method as in claim 1, wherein the contacting between the activated carbon and water having oxygen dissolved therein is carried out until the dissolved oxygen concentration in the effluent water  
5 that has been contacted with the activated carbon increases to 1 ppm or more.

7. A method as in claim 1, wherein the aqueous acrylamide solution is obtained by using a microorganisms capable of hydrating a nitrile.



European Patent  
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# EUROPEAN SEARCH REPORT

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Application number

EP 85 30 8205

| DOCUMENTS CONSIDERED TO BE RELEVANT  |   |  |   |
|--|---|--|---|
| Category   | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim                              | CLASSIFICATION OF THE APPLICATION (Int. Cl.4) |
| A  | US-A-3 947 518 (I. OSHSHIMA et al.)<br>* Claims *                             | 1  | C 07 C 103/133<br>C 07 C 102/00               |
| D, A   | FR-A-2 164 324 (MITSUI TOATSU CHEMICALS)<br>* Claims *<br><br>-----           | 1  |   |
|  |   |  | TECHNICAL FIELDS SEARCHED (Int. Cl.4)         |
|  |   |  | C 07 C 102/00<br>C 07 C 103/00                |
| The present search report has been drawn up for all claims   |   |  |   |
| Place of search<br>THE HAGUE   |   | Date of completion of the search<br>19-02-1986 | Examiner<br>MOREAU J.M.                       |
| <p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone<br/>Y : particularly relevant if combined with another document of the same category<br/>A : technological background<br/>O : non-written disclosure<br/>P : intermediate document</p> <p>T : theory or principle underlying the invention<br/>E : earlier patent document, but published on, or after the filing date<br/>D : document cited in the application<br/>L : document cited for other reasons<br/>a : member of the same patent family, corresponding document</p> |   |  |   |

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54 Method for purifying reaction solution obtained by using microbial cell, immobilized microbial cell, or immobilized enzyme.

55 A method for purifying a reaction solution obtained by using a microbial cell, an immobilized microbial cell, or an immobilized enzyme as a catalyst in a water medium is disclosed. The method comprises repeatedly filtering the reaction solution to remove fine solid matter using a polyethylene porous hollow fiber membrane having a bubble point of from 1 to 20 kg/cm<sup>2</sup>, and repeatedly washing the hollow fiber membrane before it has been clogged to such an extent that a differential pressure thereof exceeds 3 kg/cm<sup>2</sup>. By this method, a filter membrane can be repeatedly regenerated at high efficiency and can stably be used for a long period of time.

METHOD FOR PURIFYING REACTION SOLUTION  
OBTAINED BY USING MICROBIAL CELL,  
IMMOBILIZED MICROBIAL CELL, OR IMMOBILIZED ENZYME

FIELD OF THE INVENTION

This invention relates to a method of purifying a reaction solution (hereinafter, aqueous solution) obtained by using a microbial cell, an immobilized microbial cell  
5 (hereinafter, immobilized cell), or an immobilized enzyme as a catalyst in a water medium.

This invention is suitably applicable to purification of an aqueous acrylamide solution that can not be subjected to a pretreatment, such as heat treatment or acid-  
10 treatment, because of its tendency to polymerize, or cannot be treated with a coagulant, etc., to remove fine solid matters from the standpoint of product quality, and is particularly applicable to an aqueous acrylamide solution obtained by using an immobilized cell or immobilized enzyme  
15 (hereinafter, immobilized cell, etc.).

BACKGROUND OF THE INVENTION

It is known that impurities contained in an aqueous medium including fine solid matter can be removed by filtering the aqueous medium using a porous hollow fiber membrane  
20 composed of polyvinyl alcohol, and the hollow fiber membrane clogged with impurities can be regenerated for reuse by washing with an acid and/or alkali as disclosed in Japanese

Patent Publication No. 37037/83.

However, the above-described method requires a large quantity of an acid and/or alkali every time the filter is regenerated, and, therefore, involves handling of a large quantity of a highly concentrated acid or alkali waste water. In addition, the extent of restoration of filterability achieved by regeneration with an acid or alkali is not totally satisfactory. Hence, this method is not satisfactory for industrial application.

When a reaction is carried out in an aqueous medium in the presence of a microbial cell, an immobilized cell, etc., as a catalyst, the resulting aqueous solution from which the catalyst has been removed by filtration sometimes has a slight turbidity. Such turbidity should be removed before merchandising of the aqueous solution as such or in the form of a concentrate. This turbidity is attributed to fine solids suspended in the aqueous solution, and it is not easy to remove this solid matter through conventional filtration. Removal of the fine solids filtration can be achieved only with a filter membrane having a pore size as fine as 1  $\mu\text{m}$  or less, but a membrane having such a small pore size is soon clogged, and thus has a short working life.

For removing fine particles, filterability may be improved by pretreatment of the aqueous solution, such as

heat treatment and acid treatment, or addition of a coagulant to the aqueous solution. However, these techniques cannot be applied to substances that are easily polymerized or required to have high quality, such as acrylamide as described before, and removal of turbidity forms a particular subject. Although addition of a coagulant flocculates fine particles in an aqueous solution to improve filterability, a part of the coagulant added remains in the aqueous solution to deteriorate product quality.

Hence, it is keenly demanded based on industrial considerations that a clogged filter membrane be repeatedly regenerated at high efficiency so as to be used for a long period of time.

#### SUMMARY OF THE INVENTION

Accordingly, the present invention is directed to a method for purifying a reaction solution obtained by using a microbial cell, an immobilized cell, or an immobilized enzyme as a catalyst in a water medium, which comprises repeatedly filtering the reaction solution to remove fine solid matter using a polyethylene porous hollow fiber membrane having a bubble point of from 1 to 20 kg/cm<sup>2</sup> (determined in ASTM F316-70) and repeatedly washing the hollow fiber membrane before it has been clogged to such an extent that a differential pressure thereof exceeds 3 kg/cm<sup>2</sup>.

The porous hollow fiber membrane to be used in the present invention is excellent in chemical resistance as well as durability against back washing pressure or vibration repeatedly applied during washing, and, therefore, withstands repetition of filtration and washing and use for a prolonged period of time.

#### DETAILED DESCRIPTION OF THE INVENTION

The porous hollow fiber membrane which can be used in the present invention is made of polyethylene hollow fiber having a diameter of from 0.2 to 2 mm, and preferably from 0.3 to 1 mm. A preferred length of the fiber is from 40 to 200 cm from the standpoint of washing efficiency. A bundle comprising at least 100, and usually from 1,000 to 20,000 fibers is fixed to a filter. The membrane thickness provides influences on pressure resistance, trapping performance, and permeability of the membrane, and preferably ranges from 0.02 to 0.2 mm.

Fine pores of the polyethylene hollow fiber membrane have a slit shape. The pore size is expressed in terms of gas flux obtained by determining the amount of filtered air under a given pressure and bubble point (determined in ASTM F316-70) obtained by immersing a hollow fiber membrane in water, applying air pressure to the inside of the fiber and determining the pressure that generates bubbles. In the present invention, the hollow fiber membrane should have a

bubble point of from 1 to 20 kg/cm<sup>2</sup>, and preferably from 2 to 8 kg/cm<sup>2</sup>, in view of performances required to trap solid matter and to regenerate the clogged membrane. A preferred gas flux of the hollow fiber membrane is from  $8 \times 10^4$  to  $30 \times 10^4$  l/m<sup>2</sup>.hr.0.5 atm.

In carrying out the present invention, conditions for filtration of the aqueous solution and the degree of clogging of the membrane to be regenerated are important factors for lightening the labor of washing. The aqueous solution is generally filtered at a rate of from 2 to 1,000 l/m<sup>2</sup>.hr, and preferably from 10 to 200 l/m<sup>2</sup>.hr. The preferred degree of clogging of the membrane when subjected to regeneration washing is such as to have a differential pressure of from 0.5 to 3 kg/cm<sup>2</sup>, and more preferably from 0.7 to 1.2 kg/cm<sup>2</sup>. If the differential pressure of the hollow fiber membrane exceeds 3 kg/cm<sup>2</sup>, regeneration becomes difficult.

Washing of the clogged hollow fiber membrane can usually be carried out by so-called back washing, in which water is made to run in the direction opposite to the filtration direction. A greater washing effect may be obtained by passing a large quantity of water, to result in a greater differential pressure, but the differential pressure during the washing is usually set at from 1 to 10 kg/cm<sup>2</sup>, and preferably from 2 to 4 kg/cm<sup>2</sup>, from the viewpoint of dura-



bility of the hollow fiber membrane.

After repetition of regeneration by back washing several times, recovery of filterability becomes poor. If the hollow fiber membrane is exchanged with fresh one at this point, such entails cost, giving rise to a serious problem. Such a hollow fiber membrane that may not be sufficiently regenerated any longer simply by back washing, can, therefore, be subjected to chemical treatment by immersing in an alkali, an acid, an alcohol, etc., followed by back washing with water to thereby effectively remove the clogging from the membrane. Inter alia, alkali-treatment is preferred. The fact that filterability can be restored particularly by alkali-treatment is an unexpected result seeing that the fine solid matter leaked out from an immobilizing material used for immobilizing microbial cells or enzymes is generally insoluble in an alkali.

The alkali-treatment can be carried out, for example, with an aqueous sodium hydroxide solution at a concentration of from 2 to 30% by weight, and preferably from 5 to 15% by weight. A filter fitted with the hollow fiber membrane having been subjected to back washing is filled with the above-described aqueous sodium hydroxide solution and allowed to stand for from 0.1 to 100 hours, and preferably for from 1 to 40 hours. Thereafter, the membrane is back-washed with water under the same conditions as de-

scribed before. Higher alkali concentrations make the time for alkali-treatment shorter, but require greater amounts of the alkali. Accordingly, the above-recited conditions are suitable.

5 In addition, washing of a clogged hollow fiber membrane may appropriately be effected by bubbling with air, etc., or vibration by ultrasonic waves.

The present invention is preferably applied to a reaction solution obtained by using an immobilized cell or  
10 an immobilized enzyme.

The present invention will now be illustrated in greater detail with reference to the following examples, but it should be understood that these examples are not limiting the present invention. In these examples, all the parts and  
15 percents are by weight unless otherwise indicated.

#### EXAMPLE 1

A microorganism belonging to the genus Corynebacte-  
rium and capable of hydrating a nitrile, N-774 strain (FERM-  
P No. 4446), was aerobically cultivated in a medium (pH 7.2)  
20 containing 1% glucose, 0.5% peptone, 0.3% yeast extract, 0.3% malt extract, and 0.05% ferric sulfate heptahydrate. Forty parts of a washed microbial cell collected from the culture (water content: 75%), 45 parts of acrylamide, 0.5 part of N,N'-methylenebisacrylamide and 40 parts of a 0.05M  
25 phosphoric acid buffer (pH 7.7) were mixed to form a uniform

suspension. To the suspension were added 5 parts of a 5% aqueous solution of dimethylaminopropionitrile and 10 parts of a 2.5% aqueous solution of potassium persulfate, and the resulting mixture was maintained at 10°C for 30 minutes to effect polymerization. The resulting massive gel containing the microbial cell was crushed to small particles and thoroughly washed with a 0.05M phosphoric acid buffer (pH 7.7) to obtain 100 parts of an immobilized cell.

Water and acrylonitrile were reacted at 0°C in the presence of the above prepared immobilized cell in a continuous reactor equipped with a stirrer to obtain a 20% aqueous solution of acrylamide. Separation of the immobilized cell from the reaction solution was carried out by filtration using an 80 mesh metal netting and a 5- $\mu$ m-yarn reel filter. The resulting aqueous solution was found to contain 0.5 ppm of solid matter.

The resulting 20% aqueous solution of acrylamide was filtered using a polyethylene-made porous hollow fiber membrane (hollow fiber membrane: EHP 390c, a trademark of a product produced by Mitsubishi Rayon Co., Ltd.) having a filtration area of 0.3 m<sup>2</sup> and a bubble point of 4.8 kg/cm<sup>2</sup> at a rate of 8 l/hr.

When the differential pressure of the hollow fiber membrane reached about 0.9 kg/cm<sup>2</sup> due to clogging, the membrane was subjected to back washing with water at a

pressure of 4 kg/cm<sup>2</sup>, and then was reused for filtration. After the membrane was used for filtration and back-washed four times, it was immersed in a 12% aqueous solution of sodium hydroxide for 15 hours, back-washed with water, and then reused for filtration. The differential pressures across the hollow fiber membrane after the repeated filtration and regeneration as described above are shown in Table 1.

The thus obtained aqueous acrylamide solution was found to contain 0.01 ppm of a solid matter.

Table 1

|    | <u>Number of<br/>Filtration</u> | <u>Differential Pressure</u>                      |  |
|----|---------------------------------|---|--|
|    |                                 | <u>Before<br/>Washing<br/>(kg/cm<sup>2</sup>)</u> | <u>After<br/>Washing<br/>(kg/cm<sup>2</sup>)</u> |
|    | 0                               | 0.25  | -  |
|    | 1                               | 0.90  | 0.33   |
| 15 | 2                               | 0.92  | 0.36   |
|    | 3                               | 0.93  | 0.40   |
|    | 4                               | 0.95  | 0.33*  |
|    | 5                               | 0.89  | 0.35   |
|    | 6                               | 0.90  | 0.37   |
| 20 | 7                               | 0.95  | 0.40   |
|    | 8                               | 0.95  | 0.34*  |
|    | 9                               | 0.91  | 0.35   |
|    | 10                              | 0.91  | 0.37   |

|    | <u>Number of<br/>Filtration</u> | <u>Differential Pressure</u>                      |  |
|----|---------------------------------|---|--|
|    |                                 | <u>Before<br/>Washing<br/>(kg/cm<sup>2</sup>)</u> | <u>After<br/>Washing<br/>(kg/cm<sup>2</sup>)</u> |
|    | 11                              | 0.93  | 0.40   |
|    | 12                              | 0.94  | 0.34*  |
|    | 13                              | 0.90  | 0.36   |
| 5  | 14                              | 0.92  | 0.37   |
|    | 15                              | 0.92  | 0.41   |
|    | 16                              | 0.94  | 0.34*  |
|    | 17                              | 0.90  | 0.36   |
|    | 18                              | 0.91  | 0.37   |
| 10 | 19                              | 0.93  | 0.39   |
|    | 20                              | 0.95  | -  |
|    | 21                              | -   | -  |

Note: \* Alkali-treatment was performed  
in combination with back washing  
with water

#### COMPARATIVE EXAMPLE 1

15 The same procedures as described in Example 1 were repeated, except that the back washing of the clogged hollow fiber membrane was conducted every time the differential pressure of the membrane reached about 4 kg/cm<sup>2</sup>. The results obtained are shown in Table 2 below.

Table 2

|   | <u>Number of<br/>Filtration</u> | <u>Differential Pressure</u>                       |   |
|---|---------------------------------|--|---|
|   |                                 | <u>Before<br/>Washing</u><br>(kg/cm <sup>2</sup> ) | <u>After<br/>Washing</u><br>(kg/cm <sup>2</sup> ) |
|   | 0                               | 0.25   | -   |
|   | 1                               | 3.7  | 0.7   |
| 5 | 2                               | 4.0  | 1.5   |
|   | 3                               | 3.8  | 3.0   |
|   | 4                               | 3.9  | 1.5*  |
|   | 5                               | 3.9  | 3.0   |
|   | 6                               | -  | -   |

10                      Note: \* Alkali-treatment was performed  
                              in combination with back washing  
                              with water

                          According to the present invention, an aqueous  
solution having a very small content of a solid matter can  
be obtained by filtration using a polyethylene-made porous  
hollow fiber membrane.

15                      High performance filtration as demanded in the  
present invention generally involves a problem of clogging  
of a filter medium, but a combination of filtration using a  
specific filter membrane and washing under specific condi-  
tions according to the present invention makes it possible  
20                      to sufficiently restore filtrability and to thereby achieve  
stable purification of a reaction solution for a long period

of time.

Further, the present invention realizes regeneration of a filter medium by washing, for example, back washing, in combination with regeneration with chemicals, e.g., alkalis, only once per several filtration operations. As a result, amounts of chemicals to be used can be greatly reduced, and at the same time the amounts of waste water required to be handled can also be much reduced.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

## CLAIMS:

1. A method for purifying a reaction solution obtained by using a microbial cell, an immobilized microbial cell, or an immobilized enzyme as a catalyst in a water medium, which comprises repeatedly filtering the reaction solution to remove fine solid matter using a polyethylene porous, hollow fiber membrane having a bubble point of from 1 to 20 kg/cm<sup>2</sup>, and repeatedly washing the hollow fiber membrane before it has been clogged to such an extent that a differential pressure thereof exceeds 3 kg/cm<sup>2</sup>.

2. A method as in claim 1, wherein said washing is a back washing with water.

3. A method as in claim 1, wherein the method further includes alkali-treatment of the clogged hollow fiber membrane.

4. A method as in claim 1, wherein the reaction solution is an aqueous acrylamide solution.

5. A method as in claim 1, wherein the porous hollow fiber membrane has a diameter of from 0.3 to 1 mm and a length of from 40 to 200 cm.

6. A method as in claim 1, wherein the porous hollow fiber membrane has a bubble point of from 2 to 8 kg/cm<sup>2</sup>, and the hollow fiber membrane is washed when it has been clogged to such an extent that the differential pressure is from 0.7 to 1.2 kg/cm<sup>2</sup>.



7. A method as in claim 6, wherein said washing is a back washing with water.

8. A method as in claim 6, wherein the method further includes alkali-treatment of the clogged hollow fiber membrane.

9. A method as in claim 6, wherein the reaction solution is an aqueous acrylamide solution.

10. A method as in claim 6, wherein the porous hollow fiber membrane has a diameter of from 0.3 to 1 mm and a length of from 40 to 200 cm.

11. A method as in claim 1, wherein the back washing is carried out at a differential pressure of from 1 to 10 kg/cm<sup>2</sup>.

12. A method as in claim 6, wherein the back washing is carried out at a differential pressure of from 1 to 10 kg/cm<sup>2</sup>.

13. A method as in claim 3, wherein the alkali-treatment is carried out with an aqueous sodium hydroxide solution at a concentration of from 2 to 30% by weight.

14. A method as in claim 8, wherein the alkali-treatment is carried out with an aqueous sodium hydroxide solution at a concentration of from 2 to 30% by weight.

15. A method as in claim 13, wherein the alkali-treatment is carried out for a period of from 0.1 to 100 hours.

16. A method as in claim 14, wherein the alkali-treatment is carried out for a period of from 0.1 to 100 hours.